

D19



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10L 1/18, 1/22	A1	(11) International Publication Number: WO 95/29974 (43) International Publication Date: 9 November 1995 (09.11.95)
--	----	---

(21) International Application Number: PCT/US95/04981
(22) International Filing Date: 24 April 1995 (24.04.95)

(30) Priority Data: 08/236,306 2 May 1994 (02.05.94) US

(71) Applicant: CHEVRON CHEMICAL COMPANY [US/US];
P.O. Box 7141, San Francisco, CA 94120-7141 (US).

(72) Inventors: ANSARI, Matthew, H.; 882 - 26th Avenue, San Francisco, CA 94121 (US). CHERPECK, Richard, E.; 8962 Cypress Avenue, Cotati, CA 94931 (US). CHEVALIER, Randy, G.; 3115 Ellis Street, Berkeley, CA 94703 (US). TOMAN, Jeffrey, J.; 5430 Proctor Avenue, Oakland, CA 94618 (US).

(74) Agents: CAROLI, Claude, J. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).

(81) Designated States: AU, CA, CN, JP, KR, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: FUEL ADDITIVE COMPOSITIONS CONTAINING AN ALIPHATIC AMINE, A POLYOLEFIN AND A POLY(OXYALKYLENE) MONOOL

(57) Abstract

A fuel additive composition comprising: (a) a fuel-soluble aliphatic hydrocarbyl-substituted amine having at least one basic nitrogen atom wherein the hydrocarbyl group has a number average molecular weight of about 700 to 3,000; (b) a polyolefin polymer of a C₂ to C₆ monoolefin, wherein the polymer has a number average molecular weight of about 350 to 3,000; and (c) a hydrocarbyl-terminated poly(oxyalkylene) monoool having an average molecular weight of about 500 to about 5,000, wherein the oxyalkylene group is a C₂ to C₃ oxyalkylene group and the hydrocarbyl group is a C₁ to C₃₀ hydrocarbyl group.

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

FUEL ADDITIVE COMPOSITIONS CONTAINING
AN ALIPHATIC AMINE, A POLYOLEFIN
AND A POLY(OXYALKYLENE) MONOOL

BACKGROUND OF THE INVENTION

01
02
03
04
05
06
07 This invention relates to a fuel additive composition. More
08 particularly, this invention relates to a fuel additive
09 composition containing an aliphatic amine, a polyolefin and
10 a poly(oxyalkylene) monoool.

11
12 It is well known that automobile engines tend to form
13 deposits on the surface of engine components, such as
14 carburetor ports, throttle bodies, fuel injectors, intake
15 ports and intake valves, due to the oxidation and
16 polymerization of hydrocarbon fuel. These deposits, even
17 when present in relatively minor amounts, often cause
18 noticeable driveability problems, such as stalling and poor
19 acceleration. Moreover, engine deposits can significantly
20 increase an automobile's fuel consumption and production of
21 exhaust pollutants. Therefore, the development of effective
22 fuel detergents or "deposit control" additives to prevent or
23 control such deposits is of considerable importance and
24 numerous such materials are known in the art.

25
26 For example, U.S. Patent No. 3,438,757 to Honnen et al.
27 discloses branched chain aliphatic hydrocarbon N-substituted
28 amines and alkylene polyamines having a molecular weight in
29 the range of about 425 to 10,000, preferably about 450 to
30 5,000, which are useful as detergents and dispersants in
31 hydrocarbon liquid fuels for internal combustion engines.

32
33 U.S. Patent No. 3,502,451 to Moore et al. discloses motor
34 fuel compositions containing a polymer or copolymer of a C₂

01 to C₆ unsaturated hydrocarbon or the corresponding
02 hydrogenated polymer or copolymer, wherein the polymer or
03 copolymer has a molecular weight in the range of about 500
04 to 3,500. This patent further teaches that polyolefin
05 polymers of propylene and butylene are particularly
06 preferred.

07
08 U.S. Patent No. 3,700,598 to Plonsker et al. discloses
09 lubricating oil and fuel compositions containing a small
10 amount of an N-hydrocarbyl-substituted nitrilotris
11 ethylamine, wherein the hydrocarbyl group is preferably a
12 polyolefin group having a molecular weight of about 300 to
13 20,000, preferably from 500 to 2,000. This patent further
14 teaches that fuel compositions containing this additive will
15 preferably also contain a small amount of a mineral oil
16 and/or a synthetic olefin oligomer having an average
17 molecular weight of about 300 to 2,000.

18
19 U.S. Patent No. 3,756,793 to Robinson discloses a fuel
20 composition containing minor amounts of (A) a polyamine
21 which is the reaction product of a halohydrocarbon having an
22 average molecular weight between 600 to 2500 and an alkylene
23 polyamine, and (B) an organic substance having a viscosity
24 between 20 and 2500 cs. at 20°C. This patent further
25 discloses that a wide variety of compounds are suitable as
26 the organic substance, including polyamines, amides, and
27 esters or mixtures of esters, such as aliphatic diesters of
28 dibasic aliphatic carboxylic acids. Preferred materials for
29 use as the organic substance are described in this patent as
30 polymers or copolymers having an average molecular weight of
31 300 to 5,000 which are selected from hydrocarbons,
32 substituted hydrocarbons containing oxygen and substituted
33 hydrocarbons containing oxygen and nitrogen. Most preferred
34

01 polymeric compounds are described in this patent as
02 polyalkylene oxides and polyether glycols.

03
04 U.S. Patent No. 4,173,456 to Scheule et al. discloses a fuel
05 additive composition comprising (A) a hydrocarbon-soluble
06 acylated poly(alkyleneamine) and (B) a normally liquid
07 hydrocarbon-soluble polymer of a C₂ to C₆ olefin, wherein
08 the polymer has an average molecular weight of about 400 to
09 3,000.

10
11 U.S. Patent No. 4,357,148 to Graiff discloses a motor fuel
12 composition containing an octane requirement
13 increase-inhibiting amount of (a) an oil soluble aliphatic
14 polyamine containing at least one olefinic polymer chain and
15 a molecular weight of about 600 to 10,000 and (b) a polymer
16 and/or copolymer of a monoolefin having 2 to 6 carbon atoms,
17 wherein the polymer has a number average molecular weight of
18 about 500 to 1500.

19
20 U.S. Patent No. 4,832,702 to Kummer et al. discloses a fuel
21 or lubricant composition containing one or more polybutyl or
22 polyisobutylamines. This patent further discloses that,
23 since, in fuel additives, about 50% by weight of the active
24 substance can be replaced by polyisobutene without loss of
25 efficiency, the addition of polyisobutene having a molecular
26 weight of 300 to 2000, preferably from 500 to 1500, is
27 particularly advantageous from the point of view of cost.

28
29 U.S. Patent No. 5,004,478 to Vogel et al. discloses a motor
30 fuel for internal combustion engines which contains an
31 additive comprising (a) an amino- or amino-containing
32 detergent and (b) a base oil which is a mixture of (1) a
33 polyether based on propylene oxide or butylene oxide and
34

01 having a molecular weight not less than 500, and (2) an
02 ester of a monocarboxylic or polycarboxylic acid and an
03 alkanol or polyol.

04
05 U.S. Patent No. 5,089,028 to Abramo et al. discloses a fuel
06 composition containing an additive which comprises the
07 combination of (1) a polyalkenyl succinimide, (2) a
08 polyalkylene polymer, such as polyisobutylene or
09 polypropylene, (3) an ester of an aliphatic or aromatic
10 carboxylic acid, and (4) a polyether, such as polybutylene
11 oxide, polypropylene or a polybutylene/polypropylene
12 copolymer. The additive may also contain an optional amount
13 of a mineral oil or a synthetic oil.

14
15 U.S. Patent No. 5,242,469 to Sakakibara et al. discloses a
16 gasoline additive composition comprising (A) a monoester,
17 diester or polyolester, and (B) a dispersant selected from
18 (1) a monosuccinimide, (2) a bis-succinimide, (3) an
19 alkylamine having a polyolefin polymer as an alkyl group and
20 an average molecular weight of 500-5,000, and (4) a
21 benzylamine derivative having an average molecular weight of
22 500-5,000. The additive composition may additionally
23 contain a polyoxyalkylene glycol or its derivative and/or a
24 lubricant oil fraction.

25
26 PCT International Patent Application Publication
27 No. WO 92/15656, published September 17, 1992, discloses an
28 additive for gasoline petroleum fuel comprising (A) an oil
29 soluble polyolefin polyamine containing at least one
30 olefinic polymer chain, and (B) a polymer of a C₂ to C₆
31 monoolefin, wherein the polymer has a number average
32 molecular weight of up to 2,000, and preferably up to 500.
33 This document further discloses that the additive may be
34

-5-

01 used in combination with other additives, including
02 plasticizer esters, such as adipates and mixtures thereof,
03 scavengers, antioxidants, ignition improvers, and metal
04 deactivators.
05
06 European Patent Application Publication No. 0,382,159 A1,
07 published August 16, 1990, discloses a liquid hydrocarbon
08 fuel for an internal combustion engine containing a deposit
09 removing and residue inhibiting amount of at least one C₁ to
10 C₄ dialkyl ester of a C₄ to C₆ aliphatic dibasic acid.
11
12 European Patent Application Publication No. 0,356,726 A2,
13 published March 7, 1990 discloses fuel compositions
14 containing esters of aromatic di-, tri-, or tetra-carboxylic
15 acids with long-chain aliphatic alcohols or ether alcohols,
16 wherein the alcohols are produced by the hydroformylation of
17 branched olefins, and wherein the total carbon number of the
18 esters is at least 36 carbon atoms and the molecular weight
19 of the esters is 550 to 1,500, preferably 600 to 1,200.
20
21 U.S. Patent No. 4,877,416 to Campbell discloses a fuel
22 composition which contains (A) a hydrocarbyl-substituted
23 amine or polyamine having an average molecular weight of
24 about 750 to 10,000 and at least one basic nitrogen atom,
25 and (B) a hydrocarbyl-terminated poly(oxyalkylene) monool
26 having an average molecular weight of about 500 to 5,000.
27
28 It has now been discovered that the unique combination of an
29 aliphatic hydrocarbyl-substituted amine, a polyolefin
30 polymer and a poly(oxyalkylene) monool provides excellent
31 control of engine deposits, especially intake valve
32 deposits, when employed as a fuel additive composition for
33 hydrocarbon fuels.
34

-6-

SUMMARY OF THE INVENTION

01

02

03 The present invention provides a novel fuel additive
04 composition comprising:

05

06 (a) a fuel-soluble aliphatic hydrocarbyl-substituted amine
07 having at least one basic nitrogen atom wherein the
08 hydrocarbyl group has a number average molecular weight
09 of about 700 to 3,000;

10

11 (b) a polyolefin polymer of a C₂ to C₆ monoolefin, wherein
12 the polymer has a number average molecular weight of
13 about 350 to 3,000; and

14

15 (c) a hydrocarbyl-terminated poly(oxyalkylene) monool
16 having an average molecular weight of about 500 to
17 about 5,000, wherein the oxyalkylene group is a C₂ to
18 C₅ oxyalkylene group and the hydrocarbyl group is a C₁
19 to C₃₀ hydrocarbyl group.

20

21 The present invention further provides a fuel composition
22 comprising a major amount of hydrocarbons boiling in the
23 gasoline or diesel range and an effective detergent amount
24 of the novel fuel additive composition described above.

25

26 The present invention is also concerned with a fuel
27 concentrate comprising an inert stable oleophilic organic
28 solvent boiling in the range of from about 150°F to 400°F
29 and from about 10 to 70 weight percent of the fuel additive
30 composition of the instant invention.

31

32 Among other factors, the present invention is based on the
33 surprising discovery that the unique combination of an
34

-7-

01 aliphatic amine, a polyolefin and a poly(oxyalkylene) monool
02 provides unexpectedly superior deposit control performance
03 when compared to the combination of aliphatic amine and
04 either polyolefin or poly(oxyalkylene) monool alone.

05

06

DETAILED DESCRIPTION OF THE INVENTION

07

08 As noted above, the fuel additive composition of the present
09 invention contains an aliphatic hydrocarbyl-substituted
10 amine, a polyolefin polymer, and a hydrocarbyl-terminated
11 poly(oxyalkylene) monool. These compounds are described in
12 detail below.

13

14 A. The Aliphatic Hydrocarbyl-Substituted Amine

15

16 The fuel-soluble aliphatic hydrocarbyl-substituted amine
17 component of the present fuel additive composition is a
18 straight or branched chain hydrocarbyl-substituted amine
19 having at least one basic nitrogen atom wherein the
20 hydrocarbyl group has a number average molecular weight of
21 about 700 to 3,000. Typically, such aliphatic amines will
22 be of sufficient molecular weight so as to be nonvolatile at
23 normal engine intake valve operating temperatures, which are
24 generally in the range of about 175°C to 300°.

25

26 Preferably, the hydrocarbyl group will have a number average
27 molecular weight in the range of about 750 to 2,200, and
28 more preferably, in the range of about 900 to 1,500. The
29 hydrocarbyl group will generally be branched chain.

30

31 When employing a branched-chain hydrocarbyl amine, the
32 hydrocarbyl group is preferably derived from polymers of C₂
33 to C₆ olefins. Such branched-chain hydrocarbyl group will

34

01 ordinarily be prepared by polymerizing olefins of from 2 to
02 6 carbon atoms (ethylene being copolymerized with another
03 olefin so as to provide a branched-chain). The branched
04 chain hydrocarbyl group will generally have at least
05 1 branch per 6 carbon atoms along the chain, preferably at
06 least 1 branch per 4 carbon atoms along the chain and, more
07 preferably, at least 1 branch per 2 carbon atoms along the
08 chain. The preferred branched-chain hydrocarbyl groups are
09 polypropylene and polyisobutylene. The branches will
10 usually be of from 1 to 2 carbon atoms, preferably 1 carbon
11 atom, that is, methyl. In general, the branched-chain
12 hydrocarbyl group will contain from about 18 to about
13 214 carbon atoms, preferably from about 50 to about
14 157 carbon atoms.

15
16 In most instances, the branched-chain hydrocarbyl amines are
17 not a pure single product, but rather a mixture of compounds
18 having an average molecular weight. Usually, the range of
19 molecular weights will be relatively narrow and peaked near
20 the indicated molecular weight.

21
22 The amine component of the branched-chain hydrocarbyl amines
23 may be derived from ammonia, a monoamine or a polyamine.
24 The monoamine or polyamine component embodies a broad class
25 of amines having from 1 to about 12 amine nitrogen atoms and
26 from 1 to 40 carbon atoms with a carbon to nitrogen ratio
27 between about 1:1 and 10:1. Generally, the monoamine will
28 contain from 1 to about 40 carbon atoms and the polyamine
29 will contain from 2 to about 12 amine nitrogen atoms and
30 from 2 to about 40 carbon atoms. In most instances, the
31 amine component is not a pure single product, but rather a
32 mixture of compounds having a major quantity of the
33 designated amine. For the more complicated polyamines, the
34 compositions will be a mixture of amines having as the major

01 product the compound indicated and having minor amounts of
02 analogous compounds. Suitable monoamines and polyamines are
03 described more fully below.

04
05 When the amine component is a polyamine, it will preferably
06 be a polyalkylene polyamine, including alkylenediamine.
07 Preferably, the alkylene group will contain from 2 to
08 6 carbon atoms, more preferably from 2 to 3 carbon atoms.
09 Examples of such polyamines include ethylene diamine,
10 diethylene triamine, triethylene tetramine and tetraethylene
11 pentamine. Preferred polyamines are ethylene diamine and
12 diethylene triamine.

13
14 Particularly preferred branched-chain hydrocarbyl amines
15 include polyisobutenyl ethylene diamine and polyisobutyl
16 amine, wherein the polyisobutyl group is substantially
17 saturated and the amine moiety is derived from ammonia.

18
19 The aliphatic hydrocarbyl amines employed in the fuel
20 additive composition of the invention are prepared by
21 conventional procedures known in the art. Such aliphatic
22 hydrocarbyl amines and their preparations are described in
23 detail in U.S. Patent Nos. 3,438,757; 3,565,804; 3,574,576;
24 3,848,056; 3,960,515; and 4,832,702, the disclosures of
25 which are incorporated herein by reference.

26
27 Typically, the hydrocarbyl-substituted amines employed in
28 this invention are prepared by reacting a hydrocarbyl
29 halide, such as a hydrocarbyl chloride, with ammonia or a
30 primary or secondary amine to produce the hydrocarbyl-
31 substituted amine.

32
33 As noted above, the amine component of the presently
34 employed hydrocarbyl-substituted amine is derived from a

01 nitrogen-containing compound selected from ammonia, a
02 monoamine having from 1 to 40 carbon atoms, and a polyamine
03 having from 2 to about 12 amine nitrogen atoms and from 2 to
04 about 40 carbon atoms. The nitrogen-containing compound is
05 reacted with a hydrocarbyl halide to produce the
06 hydrocarbyl-substituted amine fuel additive finding use
07 within the scope of the present invention. The amine
08 component provides a hydrocarbyl amine reaction product
09 with, on average, at least about one basic nitrogen atom per
10 product molecule, i.e., a nitrogen atom titratable by a
11 strong acid.

12
13 Preferably, the amine component is derived from a polyamine
14 having from 2 to about 12 amine nitrogen atoms and from 2 to
15 about 40 carbon atoms. The polyamine preferably has a
16 carbon-to-nitrogen ratio of from about 1:1 to 10:1.

17
18 The polyamine may be substituted with substituents selected
19 from (A) hydrogen, (B) hydrocarbyl groups of from 1 to about
20 10 carbon atoms, (C) acyl groups of from 2 to about 10
21 carbon atoms, and (D) monoketo, monohydroxy, mononitro,
22 monocyano, lower alkyl and lower alkoxy derivatives of (B)
23 and (C). "Lower", as used in terms like lower alkyl or
24 lower alkoxy, means a group containing from 1 to about
25 6 carbon atoms. At least one of the substituents on one of
26 the basic nitrogen atoms of the polyamine is hydrogen, e.g.,
27 at least one of the basic nitrogen atoms of the polyamine is
28 a primary or secondary amino nitrogen.

29
30 Hydrocarbyl, as used in describing the polyamine moiety on
31 the aliphatic amine employed in this invention, denotes an
32 organic radical composed of carbon and hydrogen which may be
33 aliphatic, alicyclic, aromatic or combinations thereof,
34 e.g., aralkyl. Preferably, the hydrocarbyl group will be

-11-

01 relatively free of aliphatic unsaturation, i.e., ethylenic
02 and acetylenic, particularly acetylenic unsaturation. The
03 substituted polyamines of the present invention are
04 generally, but not necessarily, N-substituted polyamines.
05 Exemplary hydrocarbyl groups and substituted hydrocarbyl
06 groups include alkyls such as methyl, ethyl, propyl, butyl,
07 isobutyl, pentyl, hexyl, octyl, etc., alkenyls such as
08 propenyl, isobutenyl, hexenyl, octenyl, etc., hydroxyalkyls,
09 such as 2-hydroxyethyl, 3-hydroxypropyl, hydroxy-isopropyl,
10 4-hydroxybutyl, etc., ketoalkyls, such as 2-ketopropyl,
11 6-ketooctyl, etc., alkoxy and lower alkenoxy alkyls, such as
12 ethoxyethyl, ethoxypropyl, propoxyethyl, propoxypropyl,
13 diethyleneoxymethyl, triethyleneoxyethyl,
14 tetraethyleneoxyethyl, diethyleneoxyhexyl, etc. The
15 aforementioned acyl groups (C) are such as propionyl,
16 acetyl, etc. The more preferred substituents are hydrogen,
17 C₁-C₆ alkyls and C₁-C₆ hydroxyalkyls.

18
19 In a substituted polyamine, the substituents are found at
20 any atom capable of receiving them. The substituted atoms,
21 e.g., substituted nitrogen atoms, are generally
22 geometrically unequivalent, and consequently the substituted
23 amines finding use in the present invention can be mixtures
24 of mono- and poly-substituted polyamines with substituent
25 groups situated at equivalent and/or unequivalent atoms.

26
27 The more preferred polyamine finding use within the scope of
28 the present invention is a polyalkylene polyamine, including
29 alkylene diamine, and including substituted polyamines,
30 e.g., alkyl and hydroxyalkyl-substituted polyalkylene
31 polyamine. Preferably, the alkylene group contains from 2
32 to 6 carbon atoms, there being preferably from 2 to 3 carbon
33 atoms between the nitrogen atoms. Such groups are
34

-12-

01 exemplified by ethylene, 1,2-propylene, 2,2-dimethyl-
02 propylene, trimethylene, 1,3,2-hydroxypropylene, etc.
03 Examples of such polyamines include ethylene diamine,
04 diethylene triamine, di(trimethylene) triamine, dipropylene
05 triamine, triethylene tetraamine, tripropylene tetraamine,
06 tetraethylene pentamine, and pentaethylene hexamine. Such
07 amines encompass isomers such as branched-chain polyamines
08 and previously-mentioned substituted polyamines, including
09 hydroxy- and hydrocarbyl-substituted polyamines. Among the
10 polyalkylene polyamines, those containing 2-12 amino
11 nitrogen atoms and 2-24 carbon atoms are especially
12 preferred, and the C₂-C₃ alkylene polyamines are most
13 preferred, that is, ethylene diamine, polyethylene
14 polyamine, propylene diamine and polypropylene polyamine,
15 and in particular, the lower polyalkylene polyamines, e.g.,
16 ethylene diamine, dipropylene triamine, etc. Particularly
17 preferred polyalkylene polyamines are ethylene diamine and
18 diethylene triamine.

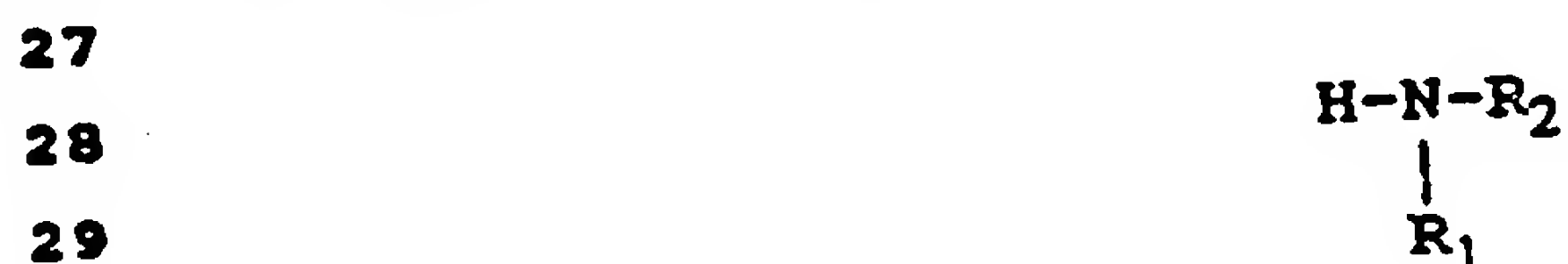
19
20 The amine component of the presently employed aliphatic
21 amine fuel additive also may be derived from heterocyclic
22 polyamines, heterocyclic substituted amines and substituted
23 heterocyclic compounds, wherein the heterocycle comprises
24 one or more 5-6 membered rings containing oxygen and/or
25 nitrogen. Such heterocyclic rings may be saturated or
26 unsaturated and substituted with groups selected from the
27 aforementioned (A), (B), (C) and (D). The heterocyclic
28 compounds are exemplified by piperazines, such as
29 2-methylpiperazine, N-(2-hydroxyethyl)-piperazine,
30 1,2-bis-(N-piperazinyl)ethane and
31 N,N'-bis(N-piperazinyl)piperazine, 2-methylimidazoline,
32 3-aminopiperidine, 3-aminopyridine, N-(3-aminopropyl)-
33
34

-13-

01 morpholine, etc. Among the heterocyclic compounds, the
02 piperazines are preferred.

03
04 Typical polyamines that can be used to form the aliphatic
05 amine additives employed in this invention by reaction with
06 a hydrocarbyl halide include the following: ethylene
07 diamine, 1,2-propylene diamine, 1,3-propylene diamine,
08 diethylene triamine, triethylene tetramine, hexamethylene
09 diamine, tetraethylene pentamine, dimethylaminopropylene
10 diamine, N-(beta-aminoethyl)piperazine, N-(beta-
11 aminoethyl)piperidine, 3-amino-N-ethylpiperidine, N-(beta-
12 aminoethyl) morpholine, N,N'-di(beta-aminoethyl)piperazine,
13 N,N'-di(beta-aminoethyl)imidazolidone-2, N-(beta-cyanoethyl)
14 ethane-1,2-diamine, 1-amino-3,6,9-triazaoctadecane,
15 1-amino-3,6-diaza-9-oxadecane, N-(beta-aminoethyl)
16 diethanolamine, N'-acetylmethyl-N-(beta-aminoethyl)
17 ethane-1,2-diamine, N-acetyl-1,2-propanediamine,
18 N-(beta-nitroethyl)-1,3-propane diamine,
19 1,3-dimethyl-5(beta-aminoethyl)hexahydrotriazine, N-(beta-
20 aminoethyl)-hexahydrotriazine, 5-(beta-aminoethyl)-
21 1,3,5-dioxazine, 2-(2-aminoethylamino)ethanol, and
22 2-[2-(2-aminoethylamino) ethylamino]ethanol.

23
24 Alternatively, the amine component of the presently employed
25 aliphatic hydrocarbyl-substituted amine may be derived from
26 an amine having the formula:



31 wherein R_1 and R_2 are independently selected from the group
32 consisting of hydrogen and hydrocarbyl of 1 to about
33 20 carbon atoms and, when taken together, R_1 and R_2 may form
34

-14-

01 one or more 5- or 6-membered rings containing up to about
02 20 carbon atoms. Preferably, R_1 is hydrogen and R_2 is a
03 hydrocarbyl group having 1 to about 10 carbon atoms. More
04 preferably, R_1 and R_2 are hydrogen. The hydrocarbyl groups
05 may be straight-chain or branched and may be aliphatic,
06 alicyclic, aromatic or combinations thereof. The
07 hydrocarbyl groups may also contain one or more oxygen
08 atoms.

09

10 An amine of the above formula is defined as a "secondary
11 amine" when both R_1 and R_2 are hydrocarbyl. When R_1 is
12 hydrogen and R_2 is hydrocarbyl, the amine is defined as a
13 "primary amine"; and when both R_1 and R_2 are hydrogen, the
14 amine is ammonia.

15

16 Primary amines useful in preparing the aliphatic
17 hydrocarbyl-substituted amine fuel additives of the present
18 invention contain 1 nitrogen atom and 1 to about 20 carbon
19 atoms, preferably 1 to 10 carbon atoms. The primary amine
20 may also contain one or more oxygen atoms.

21

22 Preferably, the hydrocarbyl group of the primary amine is
23 methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl,
24 2-hydroxyethyl or 2-methoxyethyl. More preferably, the
25 hydrocarbyl group is methyl, ethyl or propyl.

26

27 Typical primary amines are exemplified by N-methylamine,
28 N-ethylamine, N-n-propylamine, N-isopropylamine,
29 N-n-butylamine, N-isobutylamine, N-sec-butylamine,
30 N-tert-butylamine, N-n-pentylamine, N-cyclopentylamine,
31 N-n-hexylamine, N-cyclohexylamine, N-octylamine,
32 N-decylamine, N-dodecylamine, N-octadecylamine,
33 N-benzylamine, N-(2-phenylethyl)amine, 2-aminoethanol,
34

-15-

01 3-amino-1-propanal, 2-(2-aminoethoxy)ethanol,
02 N-(2-methoxyethyl)amine, N-(2-ethoxyethyl)amine, and the
03 like. Preferred primary amines are N-methylamine,
04 N-ethylamine and N-n-propylamine.

05

06 The amine component of the presently employed aliphatic
07 hydrocarbyl-substituted amine fuel additive may also be
08 derived from a secondary amine. The hydrocarbyl groups of
09 the secondary amine may be the same or different and will
10 generally contain 1 to about 20 carbon atoms, preferably 1
11 to about 10 carbon atoms. One or both of the hydrocarbyl
12 groups may also contain one or more oxygen atoms.

13

14 Preferably, the hydrocarbyl groups of the secondary amine
15 are independently selected from the group consisting of
16 methyl, ethyl, propyl, butyl, pentyl, hexyl, 2-hydroxyethyl
17 and 2-methoxyethyl. More preferably, the hydrocarbyl groups
18 are methyl, ethyl or propyl.

19

20 Typical secondary amines which may be used in this invention
21 include N,N-dimethylamine, N,N-diethylamine, N,N-di-n-
22 propylamine, N,N-diisopropylamine, N,N-di-n-butylamine,
23 N,N-di-sec-butylamine, N,N-di-n-pentylamine, N,N-di-n-
24 hexylamine, N,N-dicyclohexylamine, N,N-dioctylamine,
25 N-ethyl-N-methylamine, N-methyl-N-n-propylamine, N-n-butyl-
26 N-methylamine, N-methyl-N-octylamine, N-ethyl-N-
27 isopropylamine, N-ethyl-N-octylamine, N,N-di(2-
28 hydroxyethyl)amine, N,N-di(3-hydroxypropyl)amine,
29 N,N-di(ethoxyethyl)amine, N,N-di(propoxyethyl)amine, and the
30 like. Preferred secondary amines are N,N-dimethylamine,
31 N,N-diethylamine and N,N-di-n-propylamine.

32

33 Cyclic secondary amines may also be employed to form the
34 aliphatic amine additives of this invention. In such cyclic

-16-

01 compounds, R_1 and R_2 of the formula hereinabove, when taken
02 together, form one or more 5- or 6-membered rings containing
03 up to about 20 carbon atoms. The ring containing the amine
04 nitrogen atom is generally saturated, but may be fused to
05 one or more saturated or unsaturated rings. The rings may
06 be substituted with hydrocarbyl groups of from 1 to about
07 10 carbon atoms and may contain one or more oxygen atoms.

08

09 Suitable cyclic secondary amines include piperidine,
10 4-methylpiperidine, pyrrolidine, morpholine,
11 2,6-dimethylmorpholine, and the like.

12

13 In many instances, the amine component is not a single
14 compound but a mixture in which one or several compounds
15 predominate with the average composition indicated. For
16 example, tetraethylene pentamine prepared by the
17 polymerization of aziridine or the reaction of
18 dichloroethylene and ammonia will have both lower and higher
19 amine members, e.g., triethylene tetraamine, substituted
20 piperazines and pentaethylene hexamine, but the composition
21 will be mainly tetraethylene pentamine and the empirical
22 formula of the total amine composition will closely
23 approximate that of tetraethylene pentamine. Finally, in
24 preparing the compounds of this invention using a polyamine,
25 where the various nitrogen atoms of the polyamine are not
26 geometrically equivalent, several substitutional isomers are
27 possible and are encompassed within the final product.

28 Methods of preparation of amines and their reactions are
29 detailed in Sidgwick's "The Organic Chemistry of Nitrogen",
30 Clarendon Press, Oxford, 1966; Noller's "Chemistry of
31 Organic Compounds", Saunders, Philadelphia, 2nd Ed., 1957;
32 and Kirk-Othmer's "Encyclopedia of Chemical Technology",
33 2nd Ed., especially Volume 2, pp. 99-116.

34

-17-

01 Preferred aliphatic hydrocarbyl-substituted amines suitable
02 for use in the present invention are hydrocarbyl-substituted
03 polyalkylene polyamines having the formula:



06
07 wherein R_3 is a hydrocarbyl group having a number average
08 molecular weight of about 700 to 3,000; R_4 is alkylene of
09 from 2 to 6 carbon atoms; and n is an integer of from 0 to
10 about 10.

11
12 Preferably, R_3 is a hydrocarbyl group having a number
13 average molecular weight of about 750 to 2,200, more
14 preferably, from about 900 to 1,500. Preferably, R_4 is
15 alkylene of from 2 to 3 carbon atoms and n is preferably an
16 integer of from 1 to 6.

17
18 B. The Polyolefin Polymer

19
20 The polyolefin polymer component of the present fuel
21 additive composition is a polyolefin polymer of a C_2 to C_6
22 monoolefin, wherein the polyolefin polymer has a number
23 average molecular weight of about 350 to 3,000. The
24 polyolefin polymer may be a homopolymer or a copolymer.
25 Block copolymers are also suitable for use in this
26 invention.

27
28 In general, the polyolefin polymer will have a number
29 average molecular weight of about 350 to 3,000, preferably
30 about 350 to 1,500, and more preferably from about 350 to
31 500. Particularly preferred polyolefin polymers will have a
32 number average molecular weight of about 375 to 450.

33
34

-18-

01 The polyolefin polymers employed in the present invention
02 are generally polyolefins which are polymers or copolymers
03 of mono-olefins, particularly 1-mono-olefins, such as
04 ethylene, propylene, butylene, and the like. Preferably,
05 the mono-olefin employed will have 2 to about 4 carbon
06 atoms, and more preferably, about 3 to 4 carbon atoms. More
07 preferred mono-olefins include propylene and butylene,
08 particularly isobutylene. Polyolefins prepared from such
09 mono-olefins include polypropylene and polybutene,
10 especially polyisobutene.

11
12 The polyisobutenes which are suitable for use in the present
13 invention include polyisobutenes which comprise at least
14 about 20% of the more reactive methylvinylidene isomer,
15 preferably at least 50% and more preferably at least 70%.
16 Suitable polyisobutenes include those prepared using BF_3
17 catalysts. The preparation of such polyisobutenes in which
18 the methylvinylidene isomer comprises a high percentage of
19 the total composition is described in U.S. Patent
20 Nos. 4,152,499 and 4,605,808.

21
22 Examples of suitable polyisobutenes having a high
23 alkylvinylidene content include Ultravis 30, a polyisobutene
24 having a number average molecular weight of about 1300 and a
25 methylvinylidene content of about 74%, and Ultravis 10, a
26 950 molecular weight polyisobutene having a methylvinylidene
27 content of about 76%, both available from British Petroleum.

28
29 Preferred polyisobutenes include those having a number
30 average molecular weight of about 375 to 450, such as
31 Parapol 450, a polyisobutene having a number average
32 molecular weight of about 420, available from Exxon Chemical
33 Company.

34

01 C. The Hydrocarbyl-Terminated Poly(oxyalkylene) Monool

02
03 The hydrocarbyl-terminated poly(oxyalkylene) polymers
04 employed in the present invention are monohydroxy compounds,
05 i.e., alcohols, often termed monohydroxy polyethers, or
06 polyalkylene glycol monohydrocarbylethers, or "capped"
07 poly(oxyalkylene) glycols and are to be distinguished from
08 the poly(oxyalkylene) glycols (diols), or polyols, which are
09 not hydrocarbyl-terminated, i.e., not capped. The
10 hydrocarbyl-terminated poly(oxyalkylene) alcohols are
11 produced by the addition of lower alkylene oxides, such as
12 ethylene oxide, propylene oxide, the butylene oxides, or the
13 pentylene oxides to the hydroxy compound R_5OH under
14 polymerization conditions, wherein R_5 is the hydrocarbyl
15 group which caps the poly(oxyalkylene) chain. Methods of
16 production and properties of these polymers are disclosed in
17 U.S. Patent Nos. 2,841,479 and 2,782,240 and Kirk-Othmer's
18 "Encyclopedia of Chemical Technology", 2nd Ed., Volume 19,
19 p. 507. In the polymerization reaction, a single type of
20 alkylene oxide may be employed, e.g., propylene oxide, in
21 which case the product is a homopolymer, e.g., a
22 poly(oxyalkylene) propanol. However, copolymers are equally
23 satisfactory and random copolymers are readily prepared by
24 contacting the hydroxyl-containing compound with a mixture
25 of alkylene oxides, such as a mixture of propylene and
26 butylene oxides. Block copolymers of oxyalkylene units also
27 provide satisfactory poly(oxyalkylene) polymers for the
28 practice of the present invention. Random polymers are more
29 easily prepared when the reactivities of the oxides are
30 relatively equal. In certain cases, when ethylene oxide is
31 copolymerized with other oxides, the higher reaction rate of
32 ethylene oxide makes the preparation of random copolymers
33 difficult. In either case, block copolymers can be
34

01 prepared. Block copolymers are prepared by contacting the
02 hydroxyl-containing compound with first one alkylene oxide,
03 then the others in any order, or repetitively, under
04 polymerization conditions. A particular block copolymer is
05 represented by a polymer prepared by polymerizing propylene
06 oxide on a suitable monohydroxy compound to form a
07 poly(oxypropylene) alcohol and then polymerizing butylene
08 oxide on the poly(oxyalkylene) alcohol.

09
10 In general, the poly(oxyalkylene) polymers are mixtures of
11 compounds that differ in polymer chain length. However,
12 their properties closely approximate those of the polymer
13 represented by the average composition and molecular weight.

14
15 The polyethers employed in this invention can be represented
16 by the formula:



17
18
19
20 wherein R_5 is a hydrocarbyl group of from 1 to 30 carbon
21 atoms; R_6 is a C_2 to C_5 alkylene group; and p is an integer
22 such that the molecular weight of the polyether is from
23 about 500 to about 5,000.

24
25 Preferably, R_6 is a C_3 or C_4 alkylene group.

26
27 Preferably, R_5 is a C_7 - C_{30} alkylphenyl group. Most
28 preferably, R_5 is dodecylphenyl.

29
30 Preferably, the polyether has a molecular weight of from
31 about 750 to about 3,000; and more preferably from about 900
32 to about 1,500.

33

34

-21-

Fuel Compositions

01

02

03 The fuel additive composition of the present invention will
04 generally be employed in a hydrocarbon distillate fuel
05 boiling in the gasoline or diesel range. The proper
06 concentration of this additive composition necessary in
07 order to achieve the desired detergency and dispersancy
08 varies depending upon the type of fuel employed, the
09 presence of other detergents, dispersants and other
10 additives, etc. Generally, however, from 150 to 7500 weight
11 ppm, preferably from 300 to 2500 ppm, of the present
12 additive composition per part of base fuel is needed to
13 achieve the best results.

14

15 In terms of individual components, fuel compositions
16 containing the additive compositions of the invention will
17 generally contain about 50 to 500 ppm by weight of the
18 aliphatic amine, about 50 to 1,000 ppm by weight of the
19 polyolefin, and about 50 to 1,000 ppm by weight of the
20 poly(oxyalkylene) monool. The ratio of aliphatic amine to
21 polyolefin to poly(oxyalkylene) monool
22 (amine:polyolefin:monool) will generally be in the range of
23 about 1 : 0.5 to 10 : 0.5 to 10, preferably about 1 : 1
24 to 5 : 1 to 5, and more preferably about 1:1:1.

25

26 The deposit control fuel additive composition may be
27 formulated as a concentrate, using an inert stable
28 oleophilic (i.e., dissolves in gasoline) organic solvent
29 boiling in the range of about 150°F to 400°F (about 65°C to
30 205°C). Preferably, an aliphatic or an aromatic hydrocarbon
31 solvent is used, such as benzene, toluene, xylene or
32 higher-boiling aromatics or aromatic thinners. Aliphatic
33 alcohols of about 3 to 8 carbon atoms, such as isopropanol,
34 isobutylcarbinol, n-butanol and the like, in combination

-22-

01 with hydrocarbon solvents are also suitable for use with the
02 detergent-dispersant additive. In the concentrate, the
03 amount of the present additive composition will be
04 ordinarily at least 10% by weight and generally not exceed
05 90% by weight, preferably 40 to 85 weight percent and most
06 preferably from 50 to 80 weight percent.

07
08 In gasoline fuels, other fuel additives may be employed with
09 the additives of the present invention, including, for
10 example, oxygenates, such as t-butyl methyl ether, antiknock
11 agents, such as methylcyclopentadienyl manganese
12 tricarbonyl, and other dispersants/detergents, such as
13 various hydrocarbyl amines, hydrocarbyl poly(oxyalkylene)
14 amines, or succinimides. Also included may be lead
15 scavengers, such as aryl halides, e.g., dichlorobenzene, or
16 alkyl halides, e.g., ethylene dibromide. Additionally,
17 antioxidants, metal deactivators, pour point depressants,
18 corrosion inhibitors and demulsifiers may be present. The
19 gasoline fuels may also contain amounts of other fuels such
20 as, for example, methanol.

21
22 Additional fuel additives which may be present include
23 fuel injector inhibitors, low molecular weight fuel
24 injector detergents, and carburetor detergents, such as a
25 low molecular weight hydrocarbyl amine, including
26 polyamines, having a molecular weight below 700, such as
27 oleyl amine or a low molecular weight polyisobutenyl
28 ethylene diamine, for example, where the polyisobutenyl
29 group has a number average molecular weight of about 420.

30
31 In diesel fuels, other well-known additives can be employed,
32 such as pour point depressants, flow improver, cetane
33 improvers, and the like. The diesel fuels can also include
34 other fuels such as, for example, methanol.

-23-

01 A fuel-soluble, nonvolatile carrier fluid or oil may also be
02 used with the fuel additive composition of this invention.
03 The carrier fluid is a chemically inert hydrocarbon-soluble
04 liquid vehicle which substantially increases the nonvolatile
05 residue (NVR), or solvent-free liquid fraction of the fuel
06 additive composition while not overwhelmingly contributing
07 to octane requirement increase. The carrier fluid may be a
08 natural or synthetic oil, such as mineral oil or refined
09 petroleum oils.

10

11 These carrier fluids are believed to act as a carrier for
12 the fuel additives of the present invention and to assist in
13 removing and retarding deposits. The carrier fluid may also
14 exhibit synergistic deposit control properties when used in
15 combination with a fuel additive composition of this
16 invention.

17

18 The carrier fluids are typically employed in amounts ranging
19 from about 50 to about 2000 ppm by weight of the hydrocarbon
20 fuel, preferably from 100 to 800 ppm of the fuel.

21 Preferably, the ratio of carrier fluid to deposit control
22 additive will range from about 0.5:1 to about 10:1, more
23 preferably from 1:1 to 4:1.

24

25 When employed in a fuel concentrate, carrier fluids will
26 generally be present in amounts ranging from about 10 to
27 about 60 weight percent, preferably from 20 to 40 weight
28 percent.

29

30 The following examples are presented to illustrate specific
31 embodiments of this invention and are not to be construed in
32 any way as limiting the scope of the invention.

33

34

-24-

EXAMPLESExample A101
02
03
04
05
06
07
08
09
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

An engine test was carried out using commercial regular unleaded gasoline to measure deposits on intake valves and combustion chambers using this fuel. The test engine was a 2.3 liter, Port Fuel Injected (PFI), dual spark plug, four-cylinder engine manufactured by Ford Motor Company. Major dimensions are set forth in Table 1.

Table 1
Engine Dimensions

Bore	96 mm
Stroke	79.3 mm
Displacement	2.3 liter
Compression Ratio	10.3 : 1

The test engine was operated for 100 hours (24 hours a day) on a prescribed load and speed schedule specified by the Coordinating Research Council as a standard condition for Intake Valve Deposit testing. The cycle for engine operation is set forth in Table 2.

-25-

Table 2
Engine Operating Cycle

Step	Mode	Time in Mode [minute] ¹	Engine Speed [RPM]	Manifold Pressure [mm Hg Abs.]
1	Idle	4.5	2000	223
2	Load	8.5	2800	522

¹Each step includes a 30-second transition ramp.

At the end of each test run, the intake valves were removed, washed with hexane, and weighed. The previously determined weights of the clean valves were subtracted from the weights of the valves at the end of the run. The difference between the two weights is the weight of the intake valve deposit (IVD). Also, for each cylinder, the piston top and the mating surface of the cylinder head were scraped and the deposit removed was weighed as the measure of the combustion chamber deposit (CCD). The results are set forth in Table 3 below.

Example A2

A sample fuel composition A2 was prepared by adding:

- (1) 125 ppm by weight of a dodecylphenyl-terminated poly(oxybutylene) monool having an average molecular weight of about 1500, and
- (2) 125 ppma (parts per million actives) by weight of a hydrocarbyl amine having a 1300 MW polyisobutenyl moiety and an ethylene diamine moiety

-26-

01 to the gasoline of Example A1.

02

03 The same experiment as in Example A1 was carried out using
04 this fuel composition, and the results are shown in Table 3
05 below.

06

07

Example A3

08

09 A sample fuel composition A3 was prepared by adding:

10

11 (1) 125 ppm by weight of 420 number average molecular
12 weight polyisobutene, and

13

14 (2) 125 ppma by weight of a hydrocarbyl amine having a
15 1300 MW polyisobutenyl moiety and an ethylene diamine
16 moiety

17

18 to the gasoline of Example A1.

19

20 The same experiment as in Example A1 was carried out using
21 this fuel composition, and the results are shown in Table 3
22 below.

23

24

Example A4

25

26 A sample fuel composition A4 was prepared by adding:

27

28 (1) 125 ppm by weight of 420 number average molecular
29 weight polyisobutene; and

30

31 (2) 125 ppm by weight of a dodecylphenyl-terminated
32 poly(oxybutylene) monool having an average molecular
33 weight of about 1500, and

34

-27-

01 (3) 125 ppma by weight of a hydrocarbyl amine having a
02 1300 MW polyisobutenyl moiety and an ethylene diamine
03 moiety
04

05 to the gasoline of Example A1.

06
07 The same experiment as in Example A1 was carried out using
08 this fuel composition, and the results are shown in Table 3
09 below.

10
11 Table 3
12 Ford 2.3 Liter Engine Test Results

Test Fuel Detergent Package	Average Weight per cylinder	
	IVD (mg)	CCD (mg)
Base Fuel A1	419	949
Fuel Composition A2	147	1278
Fuel Composition A3	580	1201
Fuel Composition A4	78	1190

21
22 The results in Table 3 show that the fuel additive
23 composition of the present invention (Example A4) exhibits
24 markedly improved intake valve deposit control performance,
25 when compared to the two-component additive compositions of
26 Examples A2 and A3, while maintaining a low level of
27 combustion chamber deposits.
28

29 Example B

30
31 Fuel additive compositions of the present invention are also
32 prepared which contain:
33
34

-28-

- 01 (1) 125 ppm by weight of 420 number average molecular
02 weight polyisobutene;
03
- 04 (2) 125 ppm by weight of a dodecylphenyl-terminated
05 poly(oxybutylene) monool having an average molecular
06 weight of about 1500;
07
- 08 (3) 125 ppma by weight of a hydrocarbyl amine having a
09 1300 MW polyisobutenyl moiety and an ethylene diamine
10 moiety;
11
- 12 and at least one of the following components:
13
- 14 (4) 125-250 ppm of a mineral oil carrier fluid; and/or
15
- 16 (5) 10-50 ppm, preferably 20 ppm, of a low molecular weight
17 hydrocarbyl amine carburetor or injector detergent,
18 such as oleyl amine or polyisobutenyl (420 MW) ethylene
19 diamine.
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

-29-

01 WHAT IS CLAIMED IS:

02

03 1. A fuel additive composition comprising:

04

05 (a) a fuel-soluble aliphatic hydrocarbyl-substituted
06 amine having at least one basic nitrogen atom
07 wherein the hydrocarbyl group has a number average
08 molecular weight of about 700 to 3,000;

09

10 (b) a polyolefin polymer of a C₂ to C₆ monoolefin,
11 wherein the polymer has a number average molecular
12 weight of about 350 to 3,000; and

13

14 (c) a hydrocarbyl-terminated poly(oxyalkylene) monool
15 having an average molecular weight of about 500 to
16 about 5,000, wherein the oxyalkylene group is a C₂
17 to C₅ oxyalkylene group and the hydrocarbyl group
18 is a C₁ to C₃₀ hydrocarbyl group.

19

20 2. The fuel additive composition according to Claim 1,
21 wherein the hydrocarbyl substituent on the aliphatic
22 amine of component (a) has a number average molecular
23 weight of about 750 to 2,200.

24

25 3. The fuel additive composition according to Claim 2,
26 wherein the hydrocarbyl substituent on the aliphatic
27 amine of component (a) has a number average molecular
28 weight of about 900 to 1,500.

29

30 4. The fuel additive composition according to Claim 1,
31 wherein the aliphatic amine of component (a) is a
32 branched chain hydrocarbyl-substituted amine.

33

34

-30-

- 01 5. The fuel additive composition according to Claim 4,
02 wherein the aliphatic amine of component (a) is a
03 polyisobutenyl amine.
04
- 05 6. The fuel additive composition according to Claim 4,
06 wherein the amine moiety of the aliphatic amine is
07 derived from a polyamine having from 2 to 12 amine
08 nitrogen atoms and from 2 to 40 carbon atoms.
09
- 10 7. The fuel additive composition according to Claim 6,
11 wherein the polyamine is a polyalkylene polyamine
12 having 2 to 12 amine nitrogen atoms and 2 to 24 carbon
13 atoms.
14
- 15 8. The fuel additive composition according to Claim 7,
16 wherein the polyalkylene polyamine is selected from the
17 group consisting of ethylene diamine, diethylene
18 triamine, triethylene tetramine and tetraethylene
19 pentamine.
20
- 21 9. The fuel additive composition according to Claim 8,
22 wherein the polyalkylene polyamine is ethylene diamine
23 or diethylene triamine.
24
- 25 10. The fuel additive composition according to Claim 9,
26 wherein the aliphatic amine of component (a) is a
27 polyisobutenyl ethylene diamine.
28
- 29 11. The fuel additive composition according to Claim 1,
30 wherein the polyolefin polymer of component (b) is a
31 polymer of a C₂ to C₄ monoolefin.
32
33
34

-31-

- 01 12. The fuel additive composition according to Claim 11,
02 wherein the polyolefin polymer of component (b) is
03 polypropylene or polybutene.
04
- 05 13. The fuel additive composition according to Claim 12,
06 wherein the polyolefin polymer of component (b) is
07 polyisobutene.
08
- 09 14. The fuel additive composition according to Claim 1,
10 wherein the polyolefin polymer of component (b) has a
11 number average molecular weight of about 350 to 1500.
12
- 13 15. The fuel additive composition according to Claim 14,
14 wherein the polyolefin polymer of component (b) has a
15 number average molecular weight of about 350 to 500.
16
- 17 16. The fuel additive composition according to Claim 1,
18 wherein the hydrocarbyl-terminated poly(oxyalkylene)
19 monool of component (c) has an average molecular weight
20 of about 900 to 1500.
21
- 22 17. The fuel additive composition according to Claim 1,
23 wherein the oxyalkylene group of the hydrocarbyl-
24 terminated poly(oxyalkylene) monool of component (c) is
25 a C₃ to C₄ oxyalkylene group.
26
- 27 18. The fuel additive composition according to Claim 17,
28 wherein the oxyalkylene group of the hydrocarbyl-
29 terminated poly(oxyalkylene) monool of component (c) is
30 a C₃ oxypropylene group.
31
32
33
34

-32-

- 01 19. The fuel additive composition according to Claim 17,
02 wherein the oxyalkylene group of the hydrocarbyl-
03 terminated poly(oxyalkylene) monool of component (c) is
04 a C₄ oxybutylene group.
05
- 06 20. The fuel additive composition according to Claim 1,
07 wherein the hydrocarbyl group of the hydrocarbyl-
08 terminated poly(oxyalkylene) monool of component (c) is
09 a C₇ to C₃₀ alkylphenyl group.
10
- 11 21. The fuel additive composition according to Claim 1,
12 wherein component (a) is a polyisobutenyl amine,
13 wherein the amine moiety is derived from ethylene
14 diamine or diethylene triamine, component (b) is
15 polyisobutene, and component (c) is a C₇ to C₃₀
16 alkylphenyl-terminated poly(oxybutylene) monool.
17
- 18 22. A fuel composition comprising a major amount of
19 hydrocarbons boiling in the gasoline or diesel range
20 and an effective detergent amount of an additive
21 composition comprising:
22
- 23 (a) a fuel-soluble aliphatic hydrocarbyl-substituted
24 amine having at least one basic nitrogen atom
25 wherein the hydrocarbyl group has a number average
26 molecular weight of about 700 to 3,000;
27
- 28 (b) a polyolefin polymer of a C₂ to C₆ monoolefin,
29 wherein the polymer has a number average molecular
30 weight of about 350 to 3,000; and
31
- 32 (c) a hydrocarbyl-terminated poly(oxyalkylene) monool
33 having an average molecular weight of about 500 to
34

-33-

- 01 about 5,000, wherein the oxyalkylene group is a C₂
02 to C₅ oxyalkylene group and the hydrocarbyl group
03 is a C₁ to C₃₀ hydrocarbyl group.
04
- 05 23. The fuel composition according to Claim 22, wherein the
06 hydrocarbyl substituent on the aliphatic amine of
07 component (a) has a number average molecular weight of
08 about 750 to 2,200.
09
- 10 24. The fuel composition according to Claim 23, wherein the
11 hydrocarbyl substituent on the aliphatic amine of
12 component (a) has a number average molecular weight of
13 about 900 to 1,500.
14
- 15 25. The fuel composition according to Claim 22, wherein the
16 aliphatic amine of component (a) is a branched chain
17 hydrocarbyl-substituted amine.
18
- 19 26. The fuel composition according to Claim 25, wherein the
20 aliphatic amine of component (a) is a polyisobutenyl
21 amine.
22
- 23 27. The fuel composition according to Claim 25, wherein the
24 amine moiety of the aliphatic amine is derived from a
25 polyamine having from 2 to 12 amine nitrogen atoms and
26 from 2 to 40 carbon atoms.
27
- 28 28. The fuel composition according to Claim 27, wherein the
29 polyamine is a polyalkylene polyamine having 2 to
30 12 amine nitrogen atoms and 2 to 24 carbon atoms.
31
32
33
34

-34-

- 01 29. The fuel composition according to Claim 28, wherein the
02 polyalkylene polyamine is selected from the group
03 consisting of ethylene diamine, diethylene triamine,
04 triethylene tetramine and tetraethylene pentamine.
05
- 06 30. The fuel composition according to Claim 29, wherein the
07 polyalkylene polyamine is ethylene diamine or
08 diethylene triamine.
09
- 10 31. The fuel composition according to Claim 30, wherein the
11 aliphatic amine of component (a) is a polyisobutenyl
12 ethylene diamine.
13
- 14 32. The fuel composition according to Claim 22, wherein the
15 polyolefin polymer of component (b) is a polymer of a
16 C₂ to C₄ monoolefin.
17
- 18 33. The fuel composition according to Claim 32, wherein the
19 polyolefin polymer of component (b) is polypropylene or
20 polybutene.
21
- 22 34. The fuel composition according to Claim 33, wherein the
23 polyolefin polymer of component (b) is polyisobutene.
24
- 25 35. The fuel composition according to Claim 22, wherein the
26 polyolefin polymer of component (b) has a number
27 average molecular weight of about 350 to 1500.
28
- 29 36. The fuel composition according to Claim 35, wherein the
30 polyolefin polymer of component (b) has a number
31 average molecular weight of about 350 to 500.
32
33
34

-35-

- 01 37. The fuel composition according to Claim 22, wherein the
02 hydrocarbyl-terminated poly(oxyalkylene) monool of
03 component (c) has an average molecular weight of about
04 900 to 1500.
05
- 06 38. The fuel composition according to Claim 22, wherein the
07 oxyalkylene group of the hydrocarbyl-terminated
08 poly(oxyalkylene) monool of component (c) is a C₃ to C₄
09 oxyalkylene group.
10
- 11 39. The fuel composition according to Claim 38, wherein the
12 oxyalkylene group of the hydrocarbyl-terminated
13 poly(oxyalkylene) monool of component (c) is a C₃
14 oxypropylene group.
15
- 16 40. The fuel composition according to Claim 38, wherein the
17 oxyalkylene group of the hydrocarbyl-terminated
18 poly(oxyalkylene) monool of component (c) is a C₄
19 oxybutylene group.
20
- 21 41. The fuel composition according to Claim 22, wherein the
22 hydrocarbyl group of the hydrocarbyl-terminated
23 poly(oxyalkylene) monool of component (c) is a C₇ to
24 C₃₀ alkylphenyl group.
25
- 26 42. The fuel composition according to Claim 22, wherein
27 component (a) is a polyisobutenyl amine, wherein the
28 amine moiety is derived from ethylene diamine or
29 diethylene triamine, component (b) is polyisobutene,
30 and component (c) is a C₇ to C₃₀ alkylphenyl-terminated
31 poly(oxybutylene) monool.
32
33
34

-36-

- 01 43. A fuel concentrate comprising an inert stable
02 oleophilic organic solvent boiling in the range of from
03 about 150°F to 400°F and from about 10 to 90 weight
04 percent of an additive composition comprising:
05
06 (a) a fuel-soluble aliphatic hydrocarbyl-substituted
07 amine having at least one basic nitrogen atom
08 wherein the hydrocarbyl group has a number average
09 molecular weight of about 700 to 3,000;
10
11 (b) a polyolefin polymer of a C₂ to C₆ monoolefin,
12 wherein the polymer has a number average molecular
13 weight of about 350 to 3,000; and
14
15 (c) a hydrocarbyl-terminated poly(oxyalkylene) monool
16 having an average molecular weight of about 500 to
17 about 5,000, wherein the oxyalkylene group is a C₂
18 to C₅ oxyalkylene group and the hydrocarbyl group
19 is a C₁ to C₃₀ hydrocarbyl group.
20
21 44. The fuel concentrate according to Claim 43, wherein the
22 hydrocarbyl substituent on the aliphatic amine of
23 component (a) has a number average molecular weight of
24 about 750 to 2,200.
25
26 45. The fuel concentrate according to Claim 44, wherein the
27 hydrocarbyl substituent on the aliphatic amine of
28 component (a) has a number average molecular weight of
29 about 900 to 1,500.
30
31 46. The fuel concentrate according to Claim 43, wherein the
32 aliphatic amine of component (a) is a branched chain
33 hydrocarbyl-substituted amine.
34

-37-

- 01 47. The fuel concentrate according to Claim 46, wherein the
02 aliphatic amine of component (a) is a polyisobutenyl
03 amine.
04
- 05 48. The fuel concentrate according to Claim 46, wherein the
06 amine moiety of the aliphatic amine is derived from a
07 polyamine having from 2 to 12 amine nitrogen atoms and
08 from 2 to 40 carbon atoms.
09
- 10 49. The fuel concentrate according to Claim 48, wherein the
11 polyamine is a polyalkylene polyamine having 2 to
12 12 amine nitrogen atoms and 2 to 24 carbon atoms.
13
- 14 50. The fuel concentrate according to Claim 49, wherein the
15 polyalkylene polyamine is selected from the group
16 consisting of ethylene diamine, diethylene triamine,
17 triethylene tetramine and tetraethylene pentamine.
18
- 19 51. The fuel concentrate according to Claim 50, wherein the
20 polyalkylene polyamine is ethylene diamine or
21 diethylene triamine.
22
- 23 52. The fuel concentrate according to Claim 51, wherein the
24 aliphatic amine of component (a) is a polyisobutenyl
25 ethylene diamine.
26
- 27 53. The fuel concentrate according to Claim 43, wherein the
28 polyolefin polymer of component (b) is a polymer of a
29 C₂ to C₄ monoolefin.
30
- 31 54. The fuel concentrate according to Claim 53, wherein the
32 polyolefin polymer of component (b) is polypropylene or
33 polybutene.
34

-38-

- 01 55. The fuel concentrate according to Claim 54, wherein the
02 polyolefin polymer of component (b) is polyisobutene.
03
- 04 56. The fuel concentrate according to Claim 43, wherein the
05 polyolefin polymer of component (b) has a number
06 average molecular weight of about 350 to 1500.
07
- 08 57. The fuel concentrate according to Claim 56, wherein the
09 polyolefin polymer of component (b) has a number
10 average molecular weight of about 350 to 500.
11
- 12 58. The fuel concentrate according to Claim 43, wherein the
13 hydrocarbyl-terminated poly(oxyalkylene) monool of
14 component (c) has an average molecular weight of about
15 900 to 1500.
16
- 17 59. The fuel concentrate according to Claim 43, wherein the
18 oxyalkylene group of the hydrocarbyl-terminated
19 poly(oxyalkylene) monool of component (c) is a C₃ to C₄
20 oxyalkylene group.
21
- 22 60. The fuel concentrate according to Claim 59, wherein the
23 oxyalkylene group of the hydrocarbyl-terminated
24 poly(oxyalkylene) monool of component (c) is a C₃
25 oxypropylene group.
26
- 27 61. The fuel concentrate according to Claim 59, wherein the
28 oxyalkylene group of the hydrocarbyl-terminated
29 poly(oxyalkylene) monool of component (c) is a C₄
30 oxybutylene group.
31
32
33
34

-39-

01 62. The fuel concentrate according to Claim 43, wherein the
02 hydrocarbyl group of the hydrocarbyl-terminated
03 poly(oxyalkylene) monool of component (c) is a C₇ to
04 C₃₀ alkylphenyl group.
05

06 63. The fuel concentrate according to Claim 43, wherein
07 component (a) is a polyisobutenyl amine, wherein the
08 amine moiety is derived from ethylene diamine or
09 diethylene triamine, component (b) is polyisobutene,
10 and component (c) is a C₇ to C₃₀ alkylphenyl-terminated
11 poly(oxybutylene) monool.
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/04981

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10L 1/18, 1/22

US CL : 044/412, 432

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 044/412, 432

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A, 5,006,130 (Aiello et al) 09 April 1991, see Abstract	1-63
A	US,A, 4,464,182 (Tack et al) 07 August 1984, see entire document.	1-63
A	US,A, 4,357,148 (Graiff) 02 November 1982, see claims 1-5	1-63
A	US,A, 4,125,382 (O'Brien et al) 14 November 1978, see abstract, see claim 1.	1-63
A	US,A, 3,438,757 (Honnen et al) 15 April 1969, see entire document.	1-63

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

13 JUNE 1995

Date of mailing of the international search report

14 JUL 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer
Jacqueline V. Howard
JACQUELINE V. HOWARD

Telephone No. (703) 308-2514